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THEORY OF THE ELEMENTARY PROCESSES

IN THE SPECTROPHONE

By

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I. THEORY OF THE ELEMENTARY PROCESSES IN
THE SPECTROPHONE
A. INTRODUCTION

The use of the infrared spectrophone for the determination of the
lifetime of   vibrationally excited molecules was first described by
Slobodskaya (1). This instrument consists essentially of a cell con-
taining an infrared absorbing gas; the cell is illuminated intermit-
tently with radiation corresponding to an absorption band of the gas
and the periodic variations in pressure due to alternate heating and
cooling are detected with a sensitive microphone. Changes in phase
shift of this signal, relative to the phase of the radiation, are re-
lated to the mean vibrational lifetime of the excited molecules. The
experiments of Slobodskaya were performed with various mixtures of CO_2
and air, and results were reported for both infrared fundamentals
($\omega_2 = 667$ cm^{-1} and $\omega_3 = 2350$ cm^{-1}) as well as a combination band.

An analysis of this experiment was described by Stepanov and
Girin (2), who considered a two state model of the vibrational levels
and assumed square wave excitation.

A detailed analysis of the inelastic collision process in which
vibrational energy is converted into translational energy has been given
by Schwartz, Slawsky, and Herzfeld (3), whose results indicate that the
probability of this sort of process is a very sensitive function of both
the energy of the vibrational quantum and of the reduced mass of the col-
lision. At room temperature and atmospheric pressure, the relaxation
time for this process may vary from the order of the 10^{-6} sec. for vib-
rational modes of relatively low frequency, to as high as 1 sec. for

the higher frequency modes. Relaxation times as large as the latter figure have not been observed for several reasons: in sound dispersion studies, for example, the equilibrium heat capacity due to such modes is too small to detect.

It is the purpose of the remainder of this paper to carry out an analysis of the rates of the elementary processes occurring in the spectrophone with emphasis upon the fact that the large range of the parameters, especially their sensitivity to the vibrational frequency, leads to complications in the interpretation of the observed phase shifts.

B. RATE OF CONVERSION OF RADIANT TO TRANSLATION ENERGY

It has been shown by Schwartz, Slawsky, and Herzfeld (3) that the net rate of conversion translational into vibrational energy is

$$\frac{dE_v}{dt} = \frac{1}{\tau}\left[E_v(T) - E_v\right] \tag{1}$$

where τ is a characteristic time constant measuring the life-expectancy of the excited vibrational state before its termination by an inelastic collision. E_v is the actual vibrational energy and $E_v(T)$ is the vibrational energy which would be in equilibrium with the translational energy at translational temperature, T.

The net rate of absorption of photons must now be considered. For this purpose, the Einstein coefficients are required, namely $A_{v \rightarrow v-1}$, $B_{v \rightarrow v-1}$, and $B_{v \rightarrow v+1}$, which are respectively the coefficients of spontaneous emission, induced emission, and induced absorption. Only the fundamental transitions involving unit change in the vibrational quantum number, v, are considered. These quantities are given by the following expressions,

$$A_{v \rightarrow v-1} = \frac{8\pi^2 \nu^2}{3c^3}\left(\frac{\partial \mu}{\partial Q}\right)^2 v = \alpha v \tag{2a}$$

$$B_{v \to v-1} = \frac{\pi}{3h\nu}\left(\frac{\partial \mu}{\partial Q}\right)^2 v = \beta v \qquad (2b)$$

$$B_{v \to v+1} = \frac{\pi}{3h\nu}\left(\frac{\partial \mu}{\partial Q}\right)^2 (v+1) = \beta(v+1) \qquad (2c)$$

in the case of the harmonic oscillator. The dipole derivative with respect to the normal coordinate, Q, is evaluated at equilibrium and it is assumed that only linear terms in Q appear in the expansion of μ. Now if the number of molecules per unit volume in the vibrational state v is indicated by n_v and if ρ is the density of radiation of appropriate frequency, the net rate of increase of vibrational energy, per unit volume, at the expense of radiation is

$$\frac{dE_v}{dt} = h\nu \sum_{v=0}^{\infty} \left[-(A_{v \to v-1} + B_{v \to v-1}\rho) + B_{v \to v-1}\rho \right] n_v$$

$$= h\nu \left(-\alpha \sum v n_v + \beta\rho \sum n_v \right)$$

$$= h\nu \left[-\alpha\left(\frac{E_v}{h\nu} - \frac{n}{2}\right) + \beta\rho n \right] = -\alpha E_v + h\nu\left(\frac{\alpha}{2} + \beta\rho\right)n \qquad (3)$$

In (3), n is the total number of molecules per unit volume.

In the spectrophone experiments to be considered, the radiation density, ρ , is modulated with angular frequency, ω, so that

$$\rho = \rho_0 + \rho_1 \sin \omega t + \rho_2 \sin 2\omega t + \cdots \qquad (4)$$

Although in some cases the wave form may be more nearly square than sinusoidal, the detecting device is usually sharply tuned to the fundamental modulation frequency, so that we shall be primarily concerned

with the second term in (4), and will only use the first two terms in
the following development.

By combining the expressions for interconversion of translational
and vibrational energy and for interconversion of vibrational and radiant
energy, using the modulation frequency, ω , one finds

$$\frac{dE_v}{dt} = -\left(\alpha + \frac{1}{c}\right)E_v + \frac{1}{c}E_v(T) + a_0 + a_1 \sin \omega t \tag{5}$$

where $a_0 = nh\nu \left(\frac{\alpha}{2} + \beta \varphi_0\right)$ $\tag{5a}$

$$a_1 = nh\nu \,\beta\, \varphi_1 \tag{5b}$$

If one now considers the gross heat balance in the spectrophone
cell, and allows for heat loss only by conduction, the heat flow
equation becomes

$$K \nabla^2 T - c_v \frac{\partial T}{\partial t} + \frac{1}{c}\left[E_v - E_v(T)\right] = 0 \tag{6}$$

in which K is the thermal conductivity, c_v the heat capacity (for unit
volume), and the last term represents the rate of production of sens-
ible heat by conversion of vibrational into translation energy. The
simultaneous solution of (5) and (6) is considerably simplified in
case $h\nu \gg kT$, since E_v (T) reduces to the zero point energy,
$nh\nu/2$, i.e., a constant independent of temperature and hence of the
time. Subject to such an assumption, the steady-state solution of (5)
is given by:

$$E_v = b_0 + b_1 \sin(\omega t + \phi) \tag{7}$$

with $\quad b_0 = \dfrac{nh\nu\left[\frac{1}{2}(\alpha\tau+1)+\beta\tau\rho_0\right]}{\alpha\tau+1}$ $\qquad$ (7a)

$$b_1 = \dfrac{nh\nu\,\beta\tau\rho_1}{\left[(\omega\tau)^2+(\alpha\tau+1)^2\right]^{1/2}}\qquad (7b)$$

$$= \tan^{-1}\left\{\dfrac{-\omega\tau}{\alpha\tau+1}\right\}\qquad (7c)$$

Before proceeding to a discussion of the heat flow equation, we must consider the case in which $E_v(T)$ cannot be put equal to $nh\nu/2$. Since the actual variations of T are small,

$$E_v(T) = c_v'\,\Delta T + E_v(T_0)$$

where c_v' is the vibrational heat capacity per unit volume and at constant volume, and $T = T_0 + \Delta T$. Equations (5) and (6) are replaced by

$$\dfrac{dEv}{dt} = -(\alpha+\tfrac{1}{\tau})\,E_v + \dfrac{c_v'}{\tau}\Delta T + \dfrac{E_v(To)}{\tau} + a_0 + a_1\sin\omega t\qquad (5')$$

$$\kappa\nabla^2(\Delta T) - c_v\dfrac{\partial\Delta T}{\partial t} + \dfrac{Ev}{\tau} - \dfrac{c_v'}{\tau}\Delta T - \dfrac{E_v(To)}{\tau} = 0\qquad (6')$$

A formal solution of (5') is obtained by putting

$$Ev = b_0' + b_1\sin(\omega t+\phi) + \dfrac{c_v'}{\tau}\int\Delta T\,dt$$

with $\quad b_0' = \dfrac{E_v(T_0) + nh\nu\left(\frac{\alpha\tau}{2}+\beta\tau\rho_0\right)}{\alpha\tau+1}$

C. SOLUTION OF THE HEAT FLOW EQUATION

First consider the case in which $E_v(T)$ is a constant, namely $nh\nu/2$. The heat conduction equation (6) then becomes

$$\mathcal{K} \cdot \nabla^2 T - c_v \frac{\partial T}{\partial t} + \frac{b_0}{\tau} + \frac{b_1}{\tau} \sin(\omega t + \phi) = 0 \qquad (8)$$

with the aid of (7). Again, we are interested in the steady-state, periodic solution of (8). Although various boundary values may be assumed, we shall consider only the simple one-dimensional problem, $T = T(x,t)$ with $T(o,t) = T(\ell,t) = 0$, ℓ representing the length of the cell. The assumption of a solution of the form

$$T(x,t) = f(x) + g(x) \sin(\omega t + \phi) + h(x) \overset{cos}{\cdot} (\omega t + \phi) \qquad (9)$$

together with the above boundary conditions leads to rather clumsy expressions for g and h involving linear combinations of the functions $\sinh \frac{x}{\lambda} \sin \frac{x}{\lambda}$, $\sinh \frac{x}{\lambda} \cos \frac{x}{\lambda}$, and $\cosh \frac{x}{\lambda} \sin \frac{x}{\lambda}$, where

$$\lambda^2 = \frac{2\mathcal{K}}{\omega c_v} \qquad (10)$$

The average values of $g(x)$ and $h(x)$ over the length of the cell, simplify somewhat to yield the following expressions:

$$\bar{g} = \frac{-b_1}{\omega \tau c_v} \left(\frac{\lambda}{\ell}\right) \left[\frac{\sinh \frac{\ell}{\lambda} \cos \frac{\ell}{\lambda} + \cosh \frac{\ell}{\lambda} \sin \frac{\ell}{\lambda} - \sinh \frac{\ell}{\lambda} \cosh \frac{\ell}{\lambda} - \sin \frac{\ell}{\lambda} \cos \frac{\ell}{\lambda}}{\sinh^2 \frac{\ell}{\lambda} + \sin^2 \frac{\ell}{\lambda}} \right] \quad (11)$$

$$\bar{h} = \frac{b_1}{\omega \tau c_v} \left(\frac{\lambda}{\ell}\right) \left[\frac{\sinh \frac{\ell}{\lambda} \cosh \frac{\ell}{\lambda} - \sinh \frac{\ell}{\lambda} \cos \frac{\ell}{\lambda} + \cosh \frac{\ell}{\lambda} \sin \frac{\ell}{\lambda} - \sin \frac{\ell}{\lambda} \cos \frac{\ell}{\lambda} - \frac{\ell}{\lambda}}{\sinh^2 \frac{\ell}{\lambda} + \sin^2 \frac{\ell}{\lambda}} \right] \quad (12)$$

If the condition $\ell \gg \lambda$ obtains, the expressions for $\bar{g}$ and $\bar{h}$ simplify to

$$\bar{g} \to \frac{b_1}{\omega \tau c_v} \frac{\lambda}{\ell} \ , \quad \bar{h} \to \frac{b_1}{\omega \tau c_v} \left(\frac{\lambda}{\ell} - 1\right)$$

whence it follows that the time dependent part of T, averaged over the cell length, is

$$T = \frac{b_1}{\omega \tau c_v} \left[\frac{\lambda}{\ell} \sin(\omega t + \phi) + \left(\frac{\lambda}{\ell} - 1\right) \cos(\omega t + \phi) \right] \tag{13}$$

which may finally be written in the form

$$T = \frac{b_1}{\omega \tau c_v} \left(1 - 2\frac{\lambda}{\ell} + 2\frac{\lambda^2}{\ell^2}\right)^{1/2} \sin(\omega t + \phi + \phi') \tag{14}$$

$$\phi = \tan^{-1}\left(1 - \frac{\ell}{\lambda}\right) \tag{15}$$

It is apparent that when $\ell \gg \lambda$, ϕ' will be very close to $-\pi/2$, and although λ may vary slightly if the pressure or composition of the gas in the spectrophone cell is altered, ϕ' will remain almost constant.

Turning to the case in which $E_v(T)$ is not constant, we shall neglect the dependence of phase shift upon heat conduction, which is simply equivalent to letting $K \to 0$ in (8). In such a case, the functions g and h assume the values:

$$g = \frac{\omega^2 \tau^2 \gamma b_1}{c_v\left[(\gamma - \omega^2 \tau^2)^2 + \omega^2 \tau^2 \gamma^2\right]} \tag{16}$$

$$h = \frac{(\gamma - \omega^2 \tau^2)\omega \tau b_1}{c_v\left[(\gamma - \omega^2 \tau^2)^2 + \omega^2 \tau^2 \gamma^2\right]} \tag{17}$$

in which $= c_v'/c_v$, i.e., the ratio of the vibrational heat capacity to

the translational heat capacity. Here the phase shift turns out to be

$$\phi'' = \tan^{-1}\left\{ \frac{\gamma - \omega^2 \tau^2}{\omega \tau \gamma} \right\}$$

Continuing the assumption that ω is high enough so that heat conduction does not play an important role, we now combine the results of (7), (7b), (7c), (16), and (17) to obtain an expression which gives the temperature amplitude and the overall phase shift:

$$\Delta T = \Delta T_1 \sin(\omega t + \phi)$$

in which

$$\Delta T_1 = \frac{\omega \tau n h \nu \beta \tau \rho_1}{C_V} \left[(\gamma - \omega^2 \tau^2)^2 + (\omega \tau \gamma)^2\right]^{-1/2} \left[(\omega \tau)^2 + (\alpha \tau + 1)^2\right]^{-1/2}$$

$$= \frac{\omega \tau^2}{C_V} A^* I_1 \left[(\gamma - \omega^2 \tau^2)^2 + (\omega \tau \gamma)^2\right]^{-1/2} \left[(\omega \tau)^2 + (\alpha \tau + 1)^2\right]^{-1/2} \quad (19)$$

and

$$\phi = \tan^{-1}\left\{ \frac{-\omega^2 \tau^2 \gamma + (\alpha \tau + 1)(\gamma - \omega^2 \tau^2)}{\omega \tau \left[\gamma - \omega^2 \tau^2 + (\alpha \tau + 1)\gamma\right]} \right\} \quad (20)$$

Here the integrated absorbtion coefficient, A^*, at the gas density employed, has been introduced; see Thorndike, Wells, and Wilson (5). I_1 is the intensity of the modulated radiation.

Some simplification of (20) is greatly desirable in order to relate the observed phase shift to τ. Other factors being equal, a small value of $\alpha \tau$ in comparison with unity leads to a large amplitude and to the following simplification of (20). If $\alpha \tau \ll 1$ and if $\omega^2 \tau^2 < \gamma$, (20) becomes approximately

$$\phi \approx \tan^{-1} \frac{1}{2\omega \tau} \approx \frac{\pi}{2} - 2\omega \tau$$

since $\omega \tau$ is then necessarily small compared with unity. This situation is realized experimentally for lower frequency molecular modes, say below 1000 cm^{-1}, where τ is less than 10^{-4} sec, $\gamma \approx 0.1$, with appropiate choice of ω.

For the higher frequency molecular modes, say above 2000 cm^{-1}, τ may become quite large, perhaps 10^{-2} seconds or greater. Using Eggers and Crawford's (4) value of $\dfrac{\partial \mu}{\partial Q}$ for the stretching mode of CO_2, $\alpha \tau$ would be 42.7 with $\tau = 10^{-2}$ sec. Thus, for high frequency molecular modes of high intensity, we may perhaps need to consider the case in which $\alpha \tau \gg 1$, which simplifies ϕ to

$$\phi \approx \tan^{-1} \frac{1}{\omega \tau} \approx \frac{\pi}{2} - \omega \tau$$

provided $\omega \tau \ll 1$. This latter situation is relatively unfavorable, however, for the following reasons: (i) when τ is large, a very small ω must be employed to justify the simplification of $\tan^{-1}$ just employed; (ii) this leads to relatively large conduction heat loss. In any case, it appears that Slobodskaya's (1) identification of the observed time lag with τ is not justified for the 2350 cm^{-1} band of CO_2 when a modulation frequency of $\omega = 1572$ sec.$^{-1}$ was employed.

D. CONCLUSION

It has been shown that the phase shift of the temperature variations in the spectrophone cell, averaged over the length of the cell, depends in a complex manner upon the following variables:

α = probability of spontaneous emission

γ = ratio of vibrational to translational heat capacity

ω = modulation frequency

τ = mean lifetime for inelastic collisions.

Although α and γ are known with good accuracy for the modes of vibration to be studied experimentally, it appears necessary to work under conditions such that the observed phase shift is simply related to τ:

this situation is attained experimentally most easily for low frequency molecular modes, e.g., less than 1000 cm^{-1}, or for higher frequencies in the case of collisions with very light molecules such as H_2 or He. It is further necessary that $\omega^2 \tau^2 \lesssim \gamma$. Since γ is 0.133 when the molecular frequency is 1000 cm^{-1}, and τ may be of the order 10^{-4}, ω should be less than 10^2.

When $\alpha \tau$ is much less than unity, and, in addition, $\omega^2 \tau^2 < \gamma$ the amplitude of the temperature variations reduces to

$$\Delta T_1 = \frac{\omega \tau^2 A^* I_1}{\gamma C_V}$$

and when $\alpha \tau \ll 1$, but $\omega^2 \tau^2 \gg \gamma$

$$\Delta T_1 = \frac{A^* I_1}{\omega^2 \tau C_V}$$

It is thus apparent that optimum response is obtain when $\omega \tau$ is of the order of $\gamma^{1/2}$, a condition which is somewhat in conflict with the optimum situation for a simple relation between α and τ. If γ vanishes, the response improves as ω decreases, but this conclusion, of course, neglects the effect of heat conduction, which demands that

$$\omega \gg \frac{2 K}{\ell^2 C_V}$$

for good response.

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